

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Polybutadiene Rubber Composition

We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, a Corporation organised under the Laws of Japan, of 25—1 Dojimahadori-1-chome, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a polybutadiene rubber composition in which the polybutadiene rubber contains 20—50% of a cis, 1,4-structure and less than 40% of a 1,2-structure, to a method of producing the composition, and to articles formed therefrom.

The percentage relationships of cis 1,4-structure and 1,2-structure of the polybutadiene rubber are by mol %. All other percentages and parts referred to herein are by weight.

The polybutadiene rubber used in the compositions of this invention may be manufactured using a lithium based catalyst as explained, for example, by I. Kuntz in the Journal of Polymer Science, Vol. 42, pp 299—303 (1960). However, the invention is not dependent upon the particular means by which the polybutadiene rubber having the said constitution of cis 1,4- and 1,2-structures is made.

Such a polybutadiene rubber differs in microstructure from the polybutadiene rubber manufactured using a Ziegler type catalyst and characterized by at least 75% of a cis 1,4-structure (for example, as described in British Patent Specification No. 848,065 and Belgian Patent No. 575,671). Furthermore, it differs fundamentally in microstructure from the polybutadiene rubber having less than 10% of a cis 1,4-structure which is manufactured by the emulsion polymerization using a free radical catalyst.

Generally speaking a polybutadiene rubber contains very few side chains in its molecular

structure, so its molecular interaction is weak and its processability is poor although its other practical properties are excellent. Therefore the conditions under which it is processed are usually strictly limited. Furthermore, these processing conditions vary, essentially depending on how much of a cis 1,4-structure the polybutadiene rubber contains. For example, the polybutadiene rubber containing 95.5% of a cis 1,4-structure and a Mooney viscosity of 45 (this and all Mooney viscosities referred to herein are measured at 100°C., ML<sub>1+1</sub>) which is produced by polymerizing 1,3-butadiene using a Ziegler catalyst, can be milled easily with an open roll when the surface temperature of the roll is below 50°C, while the polybutadiene rubber containing 35.5% of a cis 1,4-structure and 12.5% of a 1,2-structure, which is polymerized using a lithium based catalyst, can be milled only when the surface temperature of the roll is above 95°C.

Furthermore, the processability of the polybutadiene rubber having 20—50% of a cis 1,4-structure and less than 40% of a 1,2-structure (referred to hereinafter simply as 'polybutadiene rubber') varies widely depending on its Mooney viscosity; it can be processed easily by ordinary methods when its Mooney viscosity is below a certain value whereas it cannot be processed easily by ordinary methods when its Mooney viscosity is higher than this.

On milling polybutadiene rubber on an open roll, it is tightly banded on the roll only when the roll surface is at a high temperature, while polybutadiene rubber presents a baggy state, lifting off the surface of the roll and being processed only with difficulty, when the roll surface is below a temperature specific to the Mooney viscosity of the polybutadiene rubber.

Polybutadiene rubber having a Mooney viscosity of 35, for example, can be processed easily with an open roll when the roll is at

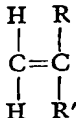
a temperature higher than 85°C, while that having a Mooney viscosity of 60 can only be processed with great difficulty unless the roll is at a temperature higher than 120°C.

5 On the other hand, when polybutadiene rubber is processed with a Banbury mixer, that having a Mooney viscosity of 35 can be processed easily, while if its Mooney viscosity is above 65 its processing becomes difficult, fillers and curing agents are not dispersed uniformly in it and the properties of its cured stocks are so poor that it is virtually useless.

10 An object of this invention is to provide a polybutadiene rubber composition of which, as compared to the polybutadiene rubber itself, the mill processability at low temperatures is improved, the dispersability therein of fillers and curing agents by means of a Banbury mixer is extremely good and the extrudability is excellent.

20 Shaped articles formed from compositions in which fillers and curing agents are mixed uniformly with the polybutadiene rubber composition of the invention, alone or together with other synthetic rubbers or natural rubber, exhibit excellent wear resistance and other practical properties.

25 According to the present invention a polybutadiene rubber composition comprises from 80 to 99 per cent by weight of polybutadiene rubber 20 to 50 per cent of which is of a cis 1,4-structure and less than 40 per cent of which is of a 1,2-structure, and from 1 to 20 per cent by weight of a polymer having a mean molecular weight of from 200 to 5,000 selected from homopolymers of alpha-olefins having the general formula



40 (wherein R and R' represent alkyl radicals having less than 6 carbon atoms or aryl radicals having less than 7 carbon atoms and one of R or R' can be a hydrogen atom), copolymers of such alpha-olefins and mixtures thereof.

45 Preferably the composition contains 85 to 95 per cent by weight of the polybutadiene rubber and 5 to 15 per cent of the olefinic hydrocarbon polymer.

50 The polybutadiene rubber composition of this invention can be produced by adding the said polymer to a polybutadiene rubber solution obtained by polymerizing butadiene with a lithium catalyst in an inert solvent or by dissolving polybutadiene rubber in an inert solvent, in the proportion of 1 to 20 per cent by weight of the said polymer relative to the total composition, mixing uniformly, removing the solvent from the solution and drying the product.

60 The polymer of the alpha-olefinic hydrocarbon can be added, as it is, at room temperature or heated at 40°—160°C, or it can be added after it has been dissolved in a suitable solvent.

65 Generally the polymer of the alpha-olefinic hydrocarbon, by virtue of its comparatively low molecular weight, is very compatible with the solution of polybutadiene rubber and can be mixed with it uniformly by stirring for a short time.

70 The polybutadiene rubber composition of this invention can also be produced by mixing polybutadiene rubber directly with the polymer of the alpha-olefinic hydrocarbon in a Banbury or other suitable mixer.

75 The effect of the polymer of the alpha-olefinic hydrocarbon added to polybutadiene rubber in improving the processability may vary, depending on its kind, molecular weight and the amount added.

80 The preferred polymers are homopolymers or copolymers of alpha-olefinic hydrocarbons of which at least one of R and R' in the above formula is an alkyl radical of up to 3 carbons or which has one benzene nucleus, for example, propylene, normal butene-1, isobutene, 2-methyl butene-1, 2-ethyl butene-1, 3-methyl butene-1, 2-methyl pentene-1, 2-ethyl pentene-1, 2-propyl pentene-1 or styrene.

85 Specific examples of such copolymers are propylene - n - butene - 1 copolymer, n - butene - 1 - isobutene copolymer and propylene-styrene copolymer.

90 The range of mean molecular weight of the alpha-olefinic hydrocarbon polymer within which the best effect of improving the processability is obtained varies with the kind of polymer. Generally, when the molecular weight of the polymer is below 200 or above 5,000, little effect is seen in improving the processability. Of the preferred polymers mentioned, those which have a mean molecular weight of about 400—3,000 have particularly desirable effects.

95 If the amount of polymer of the alpha-olefinic hydrocarbon added were less than 1 per cent, there would be little improvement in processability, whereas if more than 20 per cent were used there would be no further improvement while, in some cases, it might even cause some deterioration in the physical properties of the resultant polybutadiene rubber composition.

100 When the alpha-olefinic hydrocarbon polymer is added in an amount of 5—15 per cent based on the polybutadiene rubber composition, especially good results can be obtained.

105 Lithium based catalysts which may be used for polymerizing 1,3-butadiene for producing the poly-butadiene rubber include metallic lithium, saturated aliphatic lithium compounds such as methyl lithium, butyl lithium, amyl lithium, propyl lithium, hexyl lithium, 2-

ethylhexyl lithium and n-hexadecyl lithium, unsaturated aliphatic lithium compounds such as allyl lithium and metallyl lithium, aryl lithium compounds such as phenyl lithium, various tolyl lithiums and xylyl lithiums, alpha-naphthyl lithium, further alkaryl lithium compounds, aralkyl lithium compounds, poly-lithium compounds of hydrocarbons containing 1 to 40 carbon atoms of which a plurality of hydrogen atoms are replaced lithium atoms, such as methylene dilithium, ethylene dilithium, trimethylene dilithium, 1,2-dilithio propane, 1,4-dilithio benzene, 1,5-dilithio naphthalene, 1,2-dilithio benzene and 1,2 - dilithio - 1,2 - diphenyl ethane.

Solvents which may be used as the polymerization medium for the polybutadiene rubber include saturated hydrocarbon solvents such as pentane, hexane, heptane, cyclopentane and cyclohexane, and aromatic hydrocarbon solvents such as benzene, toluene and xylene. Solvents which may be used simply for preparing solutions of polybutadiene rubber include those mentioned above, but any solvents which can dissolve polybutadiene rubber, preferably those having a boiling point lower than 150°C can be used. The reason why a boiling point of lower than 150°C is preferable is that it is more difficult to separate the polybutadiene rubber composition of this invention from a solvent having a boiling point above that temperature.

As it has been mentioned above, the polybutadiene rubber can be polymerized from butadiene using a lithium based catalyst, but it can also be polymerized after an additive having a polar group is added, for controlling the microstructure of the polybutadiene rubber. As the additive having polar groups, diethyl ether, tetrahydrofuran, 1,3-dioxane, dibutyl thioether, pyridine, triethylamine, polyethylene oxide, polypropylene oxide and polytetramethylene oxide are preferred. A polybutadiene rubber obtained by the polymerization with an additive having a polar group has less cis 1,4-structures and more 1,2-structures than a rubber obtained without it. Although the polybutadiene rubber containing more 1,2-structures has a higher hysteresis loss and poorer dynamic properties, on the other hand, some of its physical properties such as tensile strength and tear resistance are improved, so by selecting suitable proportions of 1,2-structures, polybutadiene rubbers having very suitable properties for tyre treads and for industrial articles can be made. The maximum proportion of 1,2 structure which can be permitted without losing the desired properties of the polybutadiene rubber is 40%. Therefore the amount of additive having a polar group must be controlled so as to give a proportion of 1,2-structure not exceeding 40%.

The polybutadiene rubber compositions of this invention have excellent processability; in

particular, they can be processed easily at a high Mooney viscosity at which polybutadiene rubber not containing the polymer of the alpha-olefinic hydrocarbon could hardly be processed at all. Fillers and curing agents can be readily dispersed in the composition, and its cured stocks have excellent physical properties. Furthermore, the polybutadiene rubber compositions of this invention exhibit such good physical properties and processability that various products with useful practical properties can be made by mixing the compositions with natural rubber or synthetic rubbers such as styrene-butadiene copolymer rubber (S.B.R.) and shaping into forms products such as tyre treads, carcasses, belts, hoses and other industrial goods.

The composition ratio of the polybutadiene rubber composition of this invention and natural or synthetic rubber for producing the abovementioned cured stocks varies with the kind of final product desired, generally the polybutadiene rubber composition of this invention can constitute from 1 to 99 per cent of the total amount of rubbers present.

Rubbers which may be blended with the polybutadiene rubber compositions of this invention include natural rubber, emulsion polymerization styrene-butadiene copolymer rubber (S.B.R.), emulsion polymerisation polybutadiene rubber, butadiene - styrene copolymer rubber manufactured using a lithium based catalyst, polyisoprene rubber and various oil - extended rubbers obtained by adding oil to those rubbers. Furthermore, the compositions can also be blended for special uses with such rubbers as polychloroprene and butadiene-acrylonitrile copolymer rubber, to obtain vulcanised rubber products having useful practical properties.

The following Examples illustrate the invention.

#### EXAMPLE 1

1,3-butadiene was dissolved in refined n-hexane. To the resultant solution, 0.04 part of n-butyl lithium was added per 100 parts of 1,3-butadiene. Then the mixture was subjected to polymerization at 50°C for 5 hours. A 30% solution of polybutadiene rubber in hexane was obtained which contained 34.5% of a cis 1,4-structure and 9% of a 1,2-structure.

To this solution of polybutadiene rubber in hexane, a polymer of butene-1 (having a molecular weight of 1,500 and a viscosity of 500 centistokes at 120°C) was added in an amount of 10 parts per 100 parts of polybutadiene rubber, and uniformly mixed. Then n-hexane was removed by evaporation, leaving a polybutadiene rubber composition having a Mooney viscosity of 34.5.

For comparison, using the same method as above, a 30% solution of polybutadiene rubber in hexane was formed which contained 35.0% of a cis 1,4-structure and 10% of a 1,2-structure. By removing n-hexane from the solu-

tion by evaporation, a control polybutadiene rubber having a Mooney viscosity of 35.0 was obtained.

- 5 The polybutadiene rubber composition containing 9.1% of the polymer of butene-1 and the control polybutadiene rubber were evaluated with respect to mill processability, with the following result.

- 10 Polybutadiene rubber composition of Example 1:

banded tightly round the roll at roll temperature above 30°C.

Control polybutadiene rubber: not banded tightly on the roll at roll temperatures below 90°C.

It is evident, therefore, that the polybutadiene rubber composition containing 9.1% of the polymer of butene-1 has a much better mill processability than the control.

Next the polybutadiene rubber composition and the control were milled on open rolls with compounding ingredients according to the following formulation.

Polymer <sup>1)</sup>	100 (wt) parts
Sulphur	1.8 "
Accelerator <sup>2)</sup>	1.0 "
Stearic acid	2.0 "
Zinc oxide	5.0 "
Antioxidant <sup>3)</sup>	1.0 "
Carbon black	50.0 "
Aromatic process oil	5.0 "
Total	165.8

Notes: 1) The polybutadiene rubber composition contained polymer of butene-1.

2) N-cyclohexyl-2-benzothiazyl sulphenamide.

3) Phenyl-β-naphthylamine

- 25 The mixtures were both milled at a roll temperature of 85°C. The control was not banded tightly on the roll, and were blended with great difficulty; it took about 50 minutes to blend all the compounding ingredients completely. On the other hand, the polybutadiene rubber composition of this Example was milled while being tightly banded on the roll and did not lift off the surface of the roll even when the fillers were blended with it, so the mixing

was carried out smoothly and all the compounding ingredients were blended together uniformly in 25 minutes.

The Mooney viscosity of the polybutadiene rubber composition of this Example was 60.5 and that of the control was 60.0.

Next, a portion of each of these two compositions were extruded using a "Brabender" extruder and their extrudability was evaluated as follows:

Compounded stock		
	Polybutadiene rubber composition of this Example	Control polybutadiene rubber
Extrusion rate (cc/min)	8.5	7.5
Die swelling (%)	27.5	35.0
Extrudate appearance	good	fair

The testing conditions were as follows: extrusion temperature, 130°C; screw rotating velocity, 50 rpm; die shape, cylinder of 3 mm in diameter. Thus the polybutadiene rubber composition containing the polymer of butene-1 according to this invention is superior to the control in extrudability.

Next, portions of these two compositions were subjected to press heating at 141°C for 30 minutes and the physical properties of their cured stocks were compared; they were found to have the following properties:—

## Compounded stock

	Polybutadiene rubber composition of this Example	Control polybutadiene rubber
Tensile strength (kg/cm <sup>2</sup> ) <sup>1)</sup>	140	125
Elongation (%) <sup>2)</sup>	450	410
Stress at an elongation of 300% (kg/cm <sup>2</sup> )	95	105
Tear Strength (kg/cm) <sup>4)</sup>	50	45
Hardness (Shore A) <sup>5)</sup>	62	64

Notes: 1) Testing method ASTM D412—61T

2) „ „

3) „ „

4) „ ASTM D624—54

(Shape of the specimen: Type C)

5) Testing method ASTM D676—59T

The polybutadiene rubber composition according to this invention is evidently superior to the control in tensile strength, tear strength, and other properties.

## EXAMPLE 2

1,3-butadiene was dissolved in benzene. To the solution, 0.035 part of isobutyl lithium was added per 100 parts of 1,3-butadiene. The mixture was polymerized to 60°C for 4 hours. 25% solution of polybutadiene rubber in benzene was obtained which contained 36.5% of a cis 1,4-structure and 12.0% of a 1,2-structure.

+To the solution of polybutadiene rubber in benzene, a polymer of 2-methyl pentene-1 (having a mean molecular weight of 1,200) was added in an amount of 15 parts per 100 parts

of polybutadiene rubber, and uniformly mixed. Then benzene was removed from the solution by evaporation, leaving a polybutadiene rubber composition having a Mooney viscosity of 55.5.

For comparison, 1,3-butadiene was dissolved in benzene and polymerized with a controlled amount of isobutyl lithium. As a result, a 25% solution of polybutadiene rubber in benzene was obtained which contained 36.0% of a cis 1,4-structure and 11.0% of a 1,2-structure. From this solution benzene was removed by evaporation and a control polybutadiene rubber having a Mooney viscosity of 55.0 was obtained.

The polybutadiene rubber composition of this invention and the control polybutadiene rubber were evaluated with respect to mill processability.

## Minimum temperature of tight banding

Polybutadiene rubber composition	45°C
Control polybutadiene rubber	95°C

Thus the polybutadiene rubber composition of this invention has a substantially improved roll processability, as compared with the control.

Further, the polybutadiene rubber composition and the control polybutadiene rubber

were each blended with the following compounding ingredients, except for the sulphur and accelerator, using a Type B Banbury mixer. The blending was carried out at 140°C for 7 minutes.

10

Polymer	100 (wt) parts
Sulphur	2.2 "
Accelerator	1.2 "
Stearic acid	2.5 "
Zinc oxide	6.5 "
Antioxidant	1.5 "
Carbon black	60.0 "
Aromatic process oil	20.0 "

The blending was effected as follows:

0 minute	Charging the polymer
After 0 minute 30 seconds	Charging zinc oxide, stearic acid and antioxidant
After 1 minute	Charging half of the carbon black
After 2 minutes	Charging the rest of the carbon black
After 5 minutes	Charging aromatic process oil
After 7 minutes	Discharging

In the case of the polybutadiene rubber composition, 2 minutes after charging the first half of the carbon black, namely after a total blending time of 3 minutes, the blending torque reached a maximum, showing that blending of the polybutadiene rubber composition with carbon black was completed, whereas in the case of the control, not until 3 minutes after the first half of the carbon black was charged, namely after a total blending time of 4 minutes 30 seconds, the blending torque

reached a maximum. This indicates that the polybutadiene rubber composition has better dispersability than the rubber itself.

The sulphur and accelerator were admixed on an open roll.

The Mooney viscosity of the polybutadiene rubber composition was 60.5 and that of the control was 60.0. The properties of the cured stocks obtained by heating at 141°C for 30 minutes were as follows:

25

30

	Compounded stock	
	Polybutadiene rubber composition of this Example	Control polybutadiene rubber
Tensile strength (kg/cm <sup>2</sup> ) <sup>1</sup>		
Maximum	165	155
Minimum	140	110
Mean	155	140
Elongation (%)	450	410
Stress at an elongation of 300% (kg/cm <sup>2</sup> )	90	95
Hardness (Shore A)	60	62

Note: 1) The maximum, minimum and mean values of the 20 specimens.

- The date for the cured stocks of the control are scattered more widely than for the polybutadiene rubber composition of this Example, indicating that dispersion of carbon black and other compounding ingredients was inferior in the control.
- EXAMPLE 3
- Similarly to Example 1, polymerization was carried out using a controlled amount of catalyst. 25% solution of polybutadiene rubber in n-hexane was obtained which was divided into 6 parts. From the first part n-hexane was removed by evaporation. Polybutadiene rubber (A) having the Mooney viscosity of 45 was thus obtained.
- To each of the remaining 5 parts, a copolymer (having a mean molecular weight of 2,500) consisting of 15 parts of n-butene-1 and 85 parts of isobutene was added in the proportion indicated in the following table and then n-hexane was removed by evaporation from them to provide 5 specimens of polybutadiene rubber compositions (B)–(F).
- The Mooney viscosity and the amounts of a cis 1,4-structure and a 1,2-structure of each polybutadiene rubber composition thus obtained are also shown in the table.

		Polybutadiene rubber		Amount <sup>1</sup> of buteneisobutene copolymer added	Mooney viscosity
		cis 1,4-structure	1,2-structure		
Polybutadiene rubber	(A)	35.0	11.0	0	45.0
Polybutadiene rubber comp.	(B)	34.5	10.0	5.0	44.5
"	(C)	36.0	11.5	10.0	45.0
"	(D)	35.5	10.5	15.0	44.5
"	(E)	34.5	9.5	20.0	46.0
"	(F)	35.5	10.5	30.0	46.5

Note: 1) Weight % based on total polybutadiene rubber composition.

Next, the 6 specimens were evaluated in regard to mill banding.

		Minimum temperature of tight banding (°C)
Polybutadiene rubber	(A)	95
Polybutadiene rubber composition	(B)	65
"	(C)	35
"	(D)	25
"	(E)	25
"	(F)	25

5 Under the usual processing conditions, polybutadiene rubber compositions (B)—(D) containing 5—15% of a n-butene-1-isobutene copolymer satisfy the desired objects of the present invention.

The abovementioned specimens were milled

with a Banbury mixer according to the formulation of Example 1, and then heated at 141°C for 30 minutes. The physical properties of the cured stocks were found to be as follows. The Mooney viscosities of the products are also shown.

10

	Polybutadiene rubber (A)	(B)	Compound stock of Polybutadiene rubber comp.				(F)
	(C)	(D)	(E)				
Tensile strength (kg./cm <sup>2</sup> )	125	140	140	135	130	115	
Elongation (%)	400	440	450	440	445	450	
Stress at an elongation of 300% (kg/cm <sup>2</sup> )	105	105	100	95	92	85	
Tear strength (kg/cm)	45	50	50	45	45	35	
Hardness (Shore A)	65	62	62	60	59	57	
Unvulcanized compound Mooney viscosity	65	65	63	62	62	63.5	

20 It is evident that the polybutadiene rubber compositions (B), (C), (D) and (E) of which the contents of a n-butene-1-isobutene copolymer are within the range of this invention, are superior to the control (A) in physical properties.

25 Further, the data regarding specimen (F), a polybutadiene rubber composition containing more than 20% of a n-butene-1-isobutene copolymer, show that this has inferior physical properties.

#### EXAMPLE 4

Similarly to Example 3, polymerization was carried out using n-butyl lithium as catalyst

to produce a 25% solution of polybutadiene rubber in hexane, which was divided into 7 parts.

From the first part, n-hexane was removed by evaporation to provide a polybutadiene rubber (A) having a Mooney viscosity of 42.5. To the remaining 6 parts, 10 parts of styrene polymers of varying mean molecular weight were added per 100 parts of polybutadiene rubber. They were made into uniform solutions, from which the solvent was removed by evaporation. The Mooney viscosity and the mean molecular weight of the added styrene polymer of each polybutadiene rubber composition were as follows:

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35

40



		Mean molecular weight of added styrene polymer	Mooney viscosity
Polybutadiene rubber composition	(B)	150	35.5
"	(C)	200	35.0
"	(D)	400	35.5
"	(E)	800	36.5
"	(F)	1,500	36.0
"	(G)	5,500	35.5

Next, the 7 specimens were evaluated as regards mill banding. The results were as follows:

		Minimum temperature of tight banding (°C)
Polybutadiene rubber	(A)	85
Polybutadiene rubber composition	(B)	85
"	(C)	70
"	(D)	60
"	(E)	55
"	(F)	75
"	(G)	85

5 It is clear from the above table that the polybutadiene rubber compositions (C)—(F) of which the molecular weights of the styrene polymer are within the range specified for this invention have better mill processability than compositions (B) and (G), containing styrene polymers outside the said range.

#### EXAMPLE 5

10 Six specimens of polybutadiene rubber

polymerized using dilithiastilbene and of varying Mooney viscosity, were blended uniformly with an amorphous polypropylene (having a mean molecular weight of 3,000) in the proportions shown in the following table, 15 in a closed kneader. The blending was carried out at 105°C for 7 minutes.

The Mooney viscosity of each polybutadiene rubber composition is also shown in the following table. 20

		Amount of <sup>1)</sup> polypropylene added	Mooney viscosity of polybutadiene rubber composition
Polybutadiene rubber	(A)	0	45
Polybutadiene rubber composition	(B)	2.5	45.5
"	(C)	5.0	47.0
"	(D)	15	45.5
"	(E)	20	45.0
"	(F)	25	44.5

Note: 1) Weight %, based on total polybutadiene rubber composition.

The abovementioned specimens of polybutadiene rubber composition were blended with carbon black with a Brabender mixer (50 cc) to evaluate their dispersability. The results are shown in the following table.

The testing conditions were as follows: Temperature of the mixer, 120°C; velocity of rotation of roll, 20 rpm; amount of carbon black blended, 50 parts per 100 parts of polybutadiene rubber composition.

		Incorporation time <sup>1)</sup> (seconds)
Polybutadiene rubber	(A)	90
Polybutadiene rubber composition	(B)	90
"	(C)	80
"	(D)	50
"	(E)	45
"	(F)	45

Note: 1) Time required for achieving the maximum blending torque after charging carbon black.

It is clear from the above table that the polybutadiene rubber compositions (C)—(E) of which the contents of polypropylene are within the range of this invention have better dispersability for carbon black than controls (A) and (F). From the data for specimen (F), it is evident that increasing the content of polypropylene to more than 20% does not enhance the improvement.

Further, it is clear from the above table

that for achieving a substantial improvement in dispersability, a content of polypropylene of about 15% (Specimen (D)) is enough.

Next, for comparison, the abovementioned polybutadiene rubber (A) and polybutadiene rubber composition (B) were each mixed with compounding ingredients using a Banbury mixer according to the following formulation. The blending was carried out at 115°C for 6 minutes.

	Polybutadiene rubber composition (B)	Polybutadiene rubber (A)
Styrene-butadiene copolymer rubber	50.0	50.0
Polybutadiene rubber composition (B)	50.0	—
Polybutadiene rubber (A)	—	50.0
Sulphur	1.8	1.8
Accelerator <sup>1)</sup>	1.5	1.5
Accelerator <sup>2)</sup>	0.5	0.5
Stearic acid	2.0	2.0
Zinc oxide	5.0	5.0
Finely pulverized silica	40.0	40.0
Antioxidant <sup>3)</sup>	1.0	1.0
Process oil	5.0	5.0

- Notes: 1) Dibenzothiazyl disulphide  
 2) Diphenyl guanidine  
 3) 2.6 Ditert.-butyl hydroxytoluene

The Mooney viscosity of the compounded stock of the specimen (B) was 85.0 and that of the control (A) was 90.0. Next, these com-  
 pounded stocks were heated at 141°C for 45 minutes. The cured stocks thus obtained had the following properties.

	Compounded stock of	
	The specimen (B)	The control (A)
Tensile strength (kg/cm <sup>2</sup> )	175	155
Elongation (%)	800	750
Stress at an elongation of 300% (kg/cm <sup>2</sup> )	37	40
Tear strength (kg/cm)	45	40
Hardness (Shore A)	60	61

It is clear from the above table that the specimen (B) is superior in physical properties to a white cured stock containing 50% of S.B.R. as the polymer component.

#### EXAMPLE 6

To a 25% solution of 1,3-butadiene in n-hexane, 0.6 part of tetrahydrofuran was added per 100 parts of the solution. The polymeriza-

tion was carried out using isobutyl lithium as catalyst at 50°C for 5 hours. A solution of polybutadiene rubber was obtained which contained 27.5% of a cis 1,4-structure and 37.5% of a 1,2-structure.

To this solution of polybutadiene rubber, 10 parts of amorphous polypropylene having a mean molecular weight of 3,000 were added per 100 parts of polybutadiene rubber. From

the resultant mixture, hexane was removed by evaporation, leaving a polybutadiene rubber composition having a Mooney viscosity of 62.5.

- 5 For comparison, a solution of polybutadiene rubber was made as above but no polypropylene was added. On removing the solvent by evaporation, a polybutadiene rubber having a Mooney viscosity of 65.0 was obtained which contained 28.5% of a cis 1,4-structure and 10 35.5% of a 1,2-structure.

The polybutadiene rubber composition and the control polybutadiene rubber thus obtained

were each compounded according to the formulation and the compounding conditions of Example 2, using a Banbury mixer Type No. 15 9.

The Mooney viscosity of the compounded stock of the specimen of the Example was 84.5 and that of the control 87.5.

20 Next, one part of each compounded stock was subjected to press heating at 141°C for 30 minutes. The results were as shown in the following table.

	Compounded stock of polybutadiene rubber composition	Control polybutadiene rubber
Tensile strength (kg/cm <sup>2</sup> )	155	130
Elongation (%)	450	420
Stress at an elongation of 300% (kg/cm <sup>2</sup> )	98	105
Tear strength (kg/cm)	50	40
Hardness (Shore A)	61	62

- 25 Next, two samples of the uncured stocks were extruded into the form of tyre treads by means of an extruder. The tyre treads were fitted to green (uncured) passenger car tyres (5.60—13 in size) having carcasses which consisted of compounded stocks of styrene-butadiene copolymer (S.B.R.) and nylon tyre cord, and then they were cured under conventional conditions to make tyres. The resultant tyres fitted to passenger cars were

subjected to running tests on a paved road. 35

Eight tyres with treads of the above-mentioned compounded stock, eight with treads of the control rubber and eight standard tyres consisting of 100% butadiene-styrene copolymer tread were used for the running tests. 40 After running 20,000 km, the tyre treads were compared. The results were as shown in the following table.

	Abrasion index <sup>1)</sup>	Cracking
Tyre tread of polybutadiene rubber composition of this Example	117	Extremely slight
Standard S.B.R. tyre tread	100	Slight
Tyre tread of polybutadiene rubber of the control	105	Slight

Note: 1) The abrasion index of the standard S.B.R. is assumed as 100.

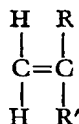
- 45 It is evident from the above table that the polybutadiene rubber composition of this invention is superior both to the control polybutadiene rubber tyre and to the standard S.B.R. tyre as regards tread performance.

#### WHAT WE CLAIM IS:—

1. A polybutadiene rubber composition comprising from 80 to 99 per cent by weight of polybutadiene rubber 20 to 50 per cent of which is of a cis 1,4-structure and less than

50

- 40 per cent of which is of a 1,2-structure, and from 1 to 20 per cent by weight of a polymer having a mean molecular weight of from 200 to 5,000 selected from homopolymers of alpha-olefins having the general formula



- (wherein R and R' represent alkyl radicals having less than 6 carbon atoms or aryl radicals having less than 7 carbon atoms and one of R or R' can be a hydrogen atom), copolymers of such alpha-olefins and mixtures thereof.

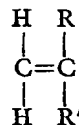
2. A polybutadiene rubber composition as claimed in Claim 1, comprising from 85 to 95 per cent by weight of the said polybutadiene rubber and from 5 to 15 per cent by weight of polypropylene having a mean molecular weight of 400 to 3,000.

3. A polybutadiene rubber composition as claimed in Claim 1, comprising from 85 to 95 per cent by weight of the said polybutadiene rubber and from 5 to 15 per cent by weight of polyisobutylene having a mean molecular weight of 400 to 3,000.

4. A polybutadiene rubber composition as claimed in Claim 1, comprising from 85 to 95 per cent by weight of the said polybutadiene rubber and from 5 to 15 per cent by weight of n-butene-1-isobutene copolymer having a mean molecular weight of 400 to 3,000.

5. A method for producing a polybutadiene rubber composition as claimed in Claim 1 which comprises adding a polymer having a mean molecular weight of from 200 to 5,000

selected from homopolymers of alpha-olefin having the general formula



(wherein R and R' are as defined in Claim 1), copolymers of such alpha-olefins or mixture thereof, to a polybutadiene rubber solution obtained by polymerizing butadiene with a lithium based catalyst in an inert solvent or by dissolving the said polybutadiene rubber in an inert solvent, in the proportion of 1 to 20 per cent by weight of the alpha-olefin polymer relative to the total composition, mixing uniformly, removing the solvent from the solution and drying the product.

6. A method for producing a polybutadiene rubber composition as claimed in Claim 1 and substantially as described in any of the Examples.

7. A polybutadiene rubber composition which has been produced by a method as claimed in Claim 5 or Claim 6.

8. A shaped article produced by shaping a polybutadiene rubber composition as claimed in any of Claims 1 to 4 or 7 and curing the shaped product.

9. A shaped article produced by blending a polybutadiene rubber composition as claimed in any of Claims 1 to 4 or 7 with a natural or synthetic rubber, shaping the resulting blend and curing the shaped product.

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